PHOTOGRAPH THIS SHEET

AD-A 951 753

DTIC ACCESSION NUMBER

LEVEL

1

INVENTORY

396/28
WP
Proj Rept #20-155

DOCUMENT IDENTIFICATION

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

Nov 12, 1951

DISTRIBUTION STATEMENT

ACCESSION FOR	
NTIS GRA&I	☑
DTIC TAB	☐
UNANNOUNCED	☐
JUSTIFICATION	
BY	
DISTRIBUTION /	
AVAILABILITY CODES	
DIST	AVAIL AND/OR SPECIAL
A	

DTIC
SELECTE
MAY 26 1982
S D
H

DATE ACCESSIONED

DTIC
COPY
INSPECTED
2

DISTRIBUTION STAMP

UNANNOUNCED

82 05 25 113

DATE RECEIVED IN DTIC

PHOTOGRAPH THIS SHEET AND RETURN TO DTIC-DDA-2

DTIC FORM 70A OCT 79

DOCUMENT PROCESSING SHEET

PROGRESS REPORT NO. 20-155

ELECTROLYTIC CONDUCTANCE OF THE TERNARY SYSTEM OF NITRIC ACID—NITROGEN DIOXIDE—WATER AT 32°F AND ATMOSPHERIC PRESSURE

GLENN D. ROBERTSON
DAVID M. MASON
B. H. SAGE

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

NOVEMBER 12, 1951

ORDCIT Project
Contract No. DA-04-495-Ord 18
Department of the Army
ORDNANCE CORPS

Progress Report No. 20-155

ELECTROLYTIC CONDUCTANCE OF THE TERNARY SYSTEM OF NITRIC ACID--NITROGEN DIOXIDE--WATER AT 32°F AND ATMOSPHERIC PRESSURE

Glenn D. Robertson
David M. Mason
B. H. Sage

B. H. Sage, *Professor*
Chemical Engineering, CIT

Louis G. Dunn, *Director*
Jet Propulsion Laboratory

Clark B. Millikan, *Chairman*
Jet Propulsion Laboratory Board

Copy No. DP 9

JET PROPULSION LABORATORY
California Institute of Technology
Pasadena, California
November 12, 1951

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION AND SUMMARY

The electrolytic conductance of the system nitric acid--nitrogen dioxide[a]--water in the liquid phase was measured at 32°F and a pressure of 1 atmosphere for compositions containing more than 80 weight per cent nitric acid.[b] The conductance of the associated binary systems nitric acid--water and nitric acid--nitrogen dioxide was measured over the entire range of compositions from 0 to 100 weight per cent nitric acid. The conductance of the binary system nitrogen dioxide--water was not measured as a result of the fact that these species undergo chemical reaction and that the rate of attainment of equilibrium is extremely slow at 32°F. The conductance measurements indicate that pure nitrogen dioxide and, as would be expected, water are relatively nonconducting, whereas nitric acid is relatively a good conductor. The addition of small quantities of nitrogen dioxide to nitric acid results in an increase in conductance. The addition of water to nitric acid results in a decrease in conductance in one range of compositions covered by this investigation. The experimental results are presented in both graphical and tabular form.

II. DESCRIPTION OF EQUIPMENT AND METHODS

Essentially the method of Kohlrausch as described by Ostwald (Cf. Ref. 1), utilizing an alternating-current Wheatstone bridge, was adopted in the present set of conductance measurements. A simplified circuit is shown in Figure 1. The unknown resistance R_x of the solution is determined when balance in the bridge circuit is obtained by adjustment of the variable resistors R_1, R_2, and R_3. A state of balance is indicated if no current flows through the current detector D when a source S of alternating voltage is applied to the system. A commercial impedance bridge was used for the variable resistors, a cathode-ray oscilloscope was employed as the current detector, and an audio oscillator furnished the source of alternating current at a frequency of 1000 cyc/sec. Direct-current measurements are precluded as a result of polarization at the electrodes.

The conductance equipment was a modified dip cell manufactured by the Central Scientific Company and had a constant of approximately 1.0 ohm-cm. The electrodes were black platinized platinum disks 0.5 inch in diameter, set 1.5 inches apart. The conductance-cell assembly shown in Figure 2 was immersed for temperature control in an ice bath located in a Dewar flask. A sample of liquid was introduced so as to fill the cell to the point A of the Pyrex receptacle shown in the Figure. The widened top portion of the vessel permitted further addition of material to the system so that a range of compositions could be obtained. As a result of appreciable changes in enthalpy for the solution, it was necessary after the mixing of materials to allow ample time for attainment of thermal equilibrium between the cell and the surrounding ice bath before conductance measurements were made. The liquid was agitated thoroughly to insure complete mixing.

---

[a]For the sake of brevity, the term nitrogen dioxide, unless otherwise specified, is used throughout this paper to designate the equilibrium mixture of nitrogen dioxide and nitrogen tetroxide.

[b]The term fuming nitric acid will be applied to the ternary system in this composition range.

The nitric acid was prepared by vacuum distillation at room temperature of a mixture of concentrated sulfuric acid and sodium nitrate. The nitric acid was collected in a receptacle at -70°F. The material collected was at least 99.9 weight per cent nitric acid as determined by an acidimetric titration. The nitric acid was stored at -10°F to reduce the thermal decomposition rate to a negligible value. Commercial nitrogen dioxide was fractionated and dried over phosphorus pentoxide. Water was redistilled from the commercial laboratory supply.

III. RESULTS

The results of the conductance measurements are depicted in Figures 3 through 5 and in Tables I through III. In Figure 3 specific conductance at 32°F is shown as a function of the weight fraction nitric acid for the binary system nitric acid--water. For comparison, measurements of conductance for this system by Veley and Manley (Cf. Ref. 2) are included in Figure 3. The experimental data for the nitric acid--water system are presented in Table I. At 32°F these components are completely miscible throughout the entire composition range. The conductance of the system increases with an increase in the weight fraction nitric acid and reaches a maximum at about 0.29 weight fraction nitric acid. Between 0.30 and 0.97 weight fraction the conductance decreases and reaches a minimum at 0.97 weight fraction nitric acid. Below 0.97 weight fraction nitric acid, hydrogen and nitrate ions are the predominant conducting species. In the range 0.97 to 1.00 weight fraction nitric acid, the conductance again increases. In this latter range, studies of the Raman spectra (Cf. Ref. 3) of the system indicate that nitric acid undergoes self-ionization to yield nitronium ions (NO_2^+) and nitrate ions (NO_3^-) according to the expression

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$

It is evident from this expression that the self-ionization of nitric acid is suppressed by the addition of water. Thus the reduction of conductance of pure nitric acid upon the addition of water may be explained.

Figure 4 presents the specific conductance at 32°F for the binary system nitric acid--nitrogen dioxide. The corresponding experimental data are recorded in Table II. At 32°F and atmospheric pressure nitrogen dioxide is miscible with nitric acid only above 0.48 weight fraction nitric acid. Below 0.48 weight fraction nitric acid a second liquid phase appears containing less than 0.1 weight per cent nitric acid. The specific conductance of this latter phase is small, being less than 7×10^{-6} $(ohm\text{-}cm)^{-1}$ at 32°F. Between 0.72 and 1.00 weight fraction nitric acid the conductance of the system decreases with increasing concentrations of acid. This behavior is in agreement with studies of Raman spectra of solutions of nitrogen dioxide in nitric acid where nitrosonium ions (NO^+) and nitrate ions (NO_3^-) have been identified (Cf. Ref. 4). The nitrogen dioxide ionizes to give these ionic species according to the expression

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

This ionization causes the increase in conductance observed when nitrogen dioxide is added to nitric acid. At weight fractions of nitric acid below 0.72, a decrease in nitric acid concentration results in a decrease in conductance until the phase boundary is reached.

In Figure 5 are shown smoothed curves of constant specific conductance as a function of composition for states greater than 0.80 weight fraction nitric acid.

These smoothed data are tabulated in Table III. The mean deviation of the conductance measurements from these data is estimated to be less than 2 per cent. From Figure 5 it is evident that conductance measurements present a possible analytical tool for determining the composition of fuming nitric acid. It is necessary to determine the concentration of only one species in the system by another physicochemical method such as the measurement of transmittance with a spectrophotometer.

The nitrogen dioxide or water concentration can be determined by transmittance measurements in the visible region or the infrared region, respectively. These measurements together with the conductance measurements establish no more than two values of composition in Figure 5. The actual composition of the sample may be determined by adding one of the components to the mixture and noting whether an increase or decrease in conductance occurs.

IV. CONCLUSION

The conductance data for a portion of the nitric acid--nitrogen dioxide--water system give additional evidence of the presence of the ionic species, nitronium, nitrosonium, and nitrate, which were indicated earlier by studies of Raman spectra (Cf. Ref. 4). A method of chemical analysis may possibly be based upon such conductance measurements. These measurements are part of an investigation of physiochemical properties which may be of value in understanding the kinetics of the thermal decomposition of fuming nitric acid and the corrosion of metals by this material.

TABLE I

EXPERIMENTAL VALUES OF SPECIFIC CONDUCTANCE OF NITRIC ACID--WATER AT 32°F AND ATMOSPHERIC PRESSURE

Nitric Acid (wt fraction)	Specific Conductance $[(ohm\text{-}cm)^{-1} \times 10^2]$	Nitric Acid (wt fraction)	Specific Conductance $[(ohm\text{-}cm)^{-1} \times 10^2]$
1.000	3.77	0.703	28.4
0.998	3.34	0.674	31.3
0.993	2.53	0.645	34.7
0.988	1.99	0.595	38.5
0.983	1.65	0.497	46.4
0.978	1.44	0.431	52.2
0.973	1.34	0.376	56.3
0.968	1.31	0.362	56.8
0.964	1.35	0.349	56.8
0.959	1.43	0.336	57.8
0.954	1.55	0.325	57.8
0.949	1.72	0.315	58.3
0.945	1.90	0.295	58.3
0.940	2.09	0.279	58.3
0.931	2.48	0.251	58.3
0.922	3.00	0.226	55.5
0.914	3.49	0.207	52.6
0.892	5.15	0.189	50.0
0.872	6.91	0.161	46.1
0.756	21.4	0.132	39.8
0.730	25.3	0.093	31.3

TABLE II

EXPERIMENTAL VALUES OF SPECIFIC CONDUCTANCE OF NITRIC ACID--NITROGEN DIOXIDE AT 32°F AND ATMOSPHERIC PRESSURE

Nitric Acid (wt fraction)	Specific Conductance $[(ohm\text{-}cm)^{-1} \times 10^2]$	Nitric Acid (wt fraction)	Specific Conductance $[(ohm\text{-}cm)^{-1} \times 10^2]$
1.000	3.41 . 07	0.800	14.6
0.980	5.00	0.751	15.2
0.971	5.83	0.707	15.3
0.962	6.53	0.642	14.7
0.952	7.20	0.581	13.6
0.942	7.91	0.529	12.5
0.916	9.60	0.489	11.7
0.890	11.2	0.451	10.7
0.856	12.9		

TABLE III

SMOOTHED VALUES OF CONDUCTANCE OF NITRIC ACID--NITROGEN DIOXIDE--WATER AT 32°F AND ATMOSPHERIC PRESSURE

Nitric Acid (wt fraction)	Specific Conductance $[(ohm\text{-}cm)^{-1} \times 10^2]$ — Nitrogen Dioxide (wt fraction)															
	0	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	0.11	0.12	0.13	0.14	0.15
1.00	3.77															
0.99	2.18	4.25														
0.98	1.51	3.2	4.90													
0.97	1.31	2.7	3.9	6.05												
0.96	1.40	2.3	3.4	4.8	6.55											
0.95	1.69	2.3	3.2	4.0	5.7	7.10										
0.94	2.07	2.7	3.2	3.9	5.0	6.4	8.10									
0.93	2.55	2.9	3.4	4.0	4.8	5.9	7.3	8.85								
0.92	3.10	3.3	3.8	4.2	4.9	5.7	6.9	8.1	8.40							
0.91	3.75	3.9	4.2	4.6	5.0	5.7	6.7	7.7	8.8	10.1						
0.90	4.52	4.7	4.8	5.0	5.3	5.9	6.6	7.4	8.3	9.5	10.6					
0.89	5.36	5.3	5.3	5.4	5.7	6.1	6.7	7.3	8.1	9.0	10.0	11.2				
0.88	6.24	6.1	6.0	6.0	6.1	6.4	6.9	7.3	8.0	8.8	9.7	10.7	11.7			
0.87	7.10	6.9	6.7	6.6	6.6	6.8	7.1	7.5	8.0	8.7	9.3	10.2	11.1	12.1		
0.86	8.00	8.0	7.6	7.2	7.1	7.2	7.4	7.7	8.2	8.7	9.2	9.9	10.8	11.7	12.6	
0.85	9.5	9.0	8.6	8.2	8.0	7.9	7.9	8.1	8.3	8.8	9.2	9.8	10.4	11.3	12.1	13.0
0.84	10.7	10.0	9.6	9.1	8.8	8.6	8.4	8.4	8.7	8.9	9.3	9.7	10.3	11.0	11.8	12.6
0.83	11.9	11.1	10.6	10.0	9.7	9.3	9.1	9.0	9.0	9.1	9.4	9.7	10.2	10.8	11.4	12.1
0.82	13.2	12.4	11.7	11.0	10.6	10.1	9.8	9.6	9.4	9.4	9.7	9.9	10.2	10.7	11.2	11.8
0.81	14.7	13.8	13.0	12.1	11.5	11.0	10.6	10.2	10.0	9.9	9.9	10.1	10.3	10.7	11.1	11.7
0.80	15.9	15.0	14.2	13.5	12.8	12.0	11.4	11.0	10.7	10.4	10.3	10.2	10.3	10.7	11.0	11.4

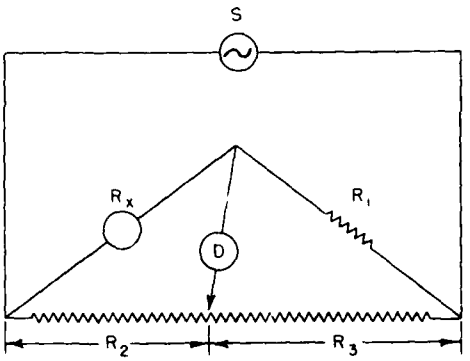

Figure 1

Wheatstone Bridge for Conductance Measurements

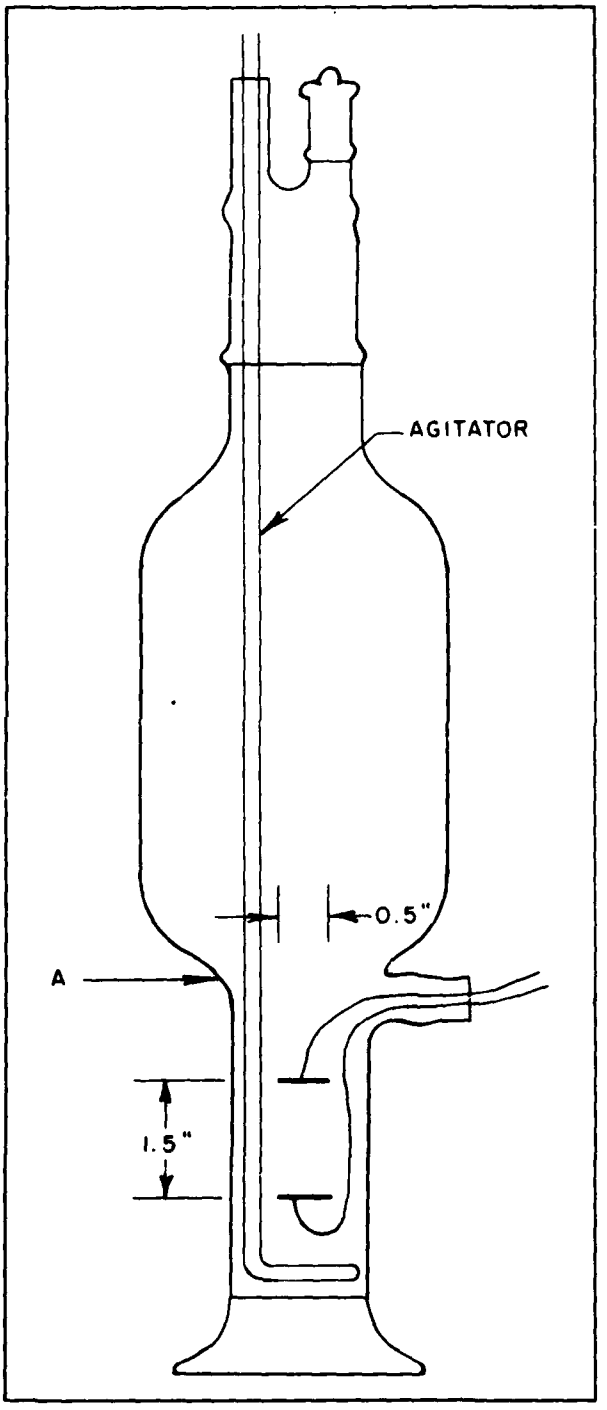

Figure 2

Conductance-Cell Assembly

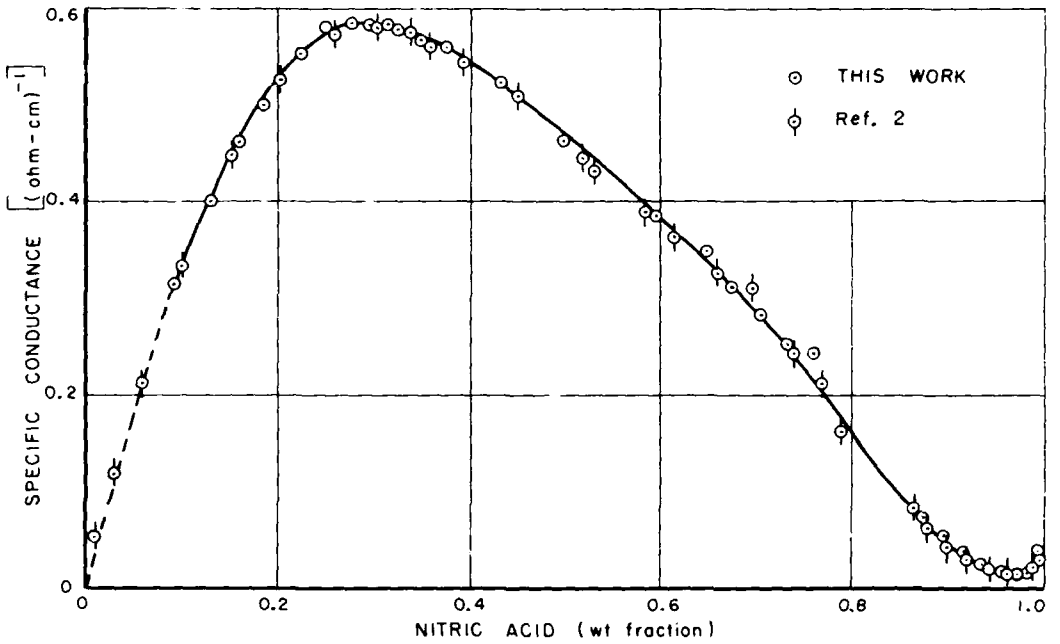

Figure 3. Specific Conductance of Nitric Acid--Water at 32°F and Atmospheric Pressure

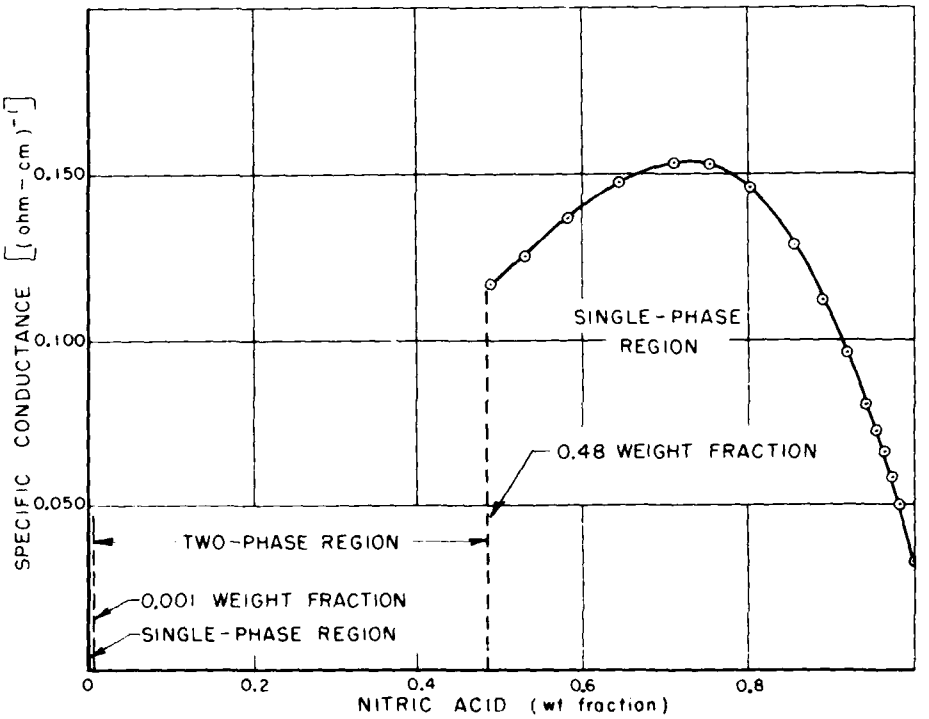

Figure 4. Specific Conductance of Nitric Acid--Nitrogen Dioxide at 32°F and Atmospheric Pressure

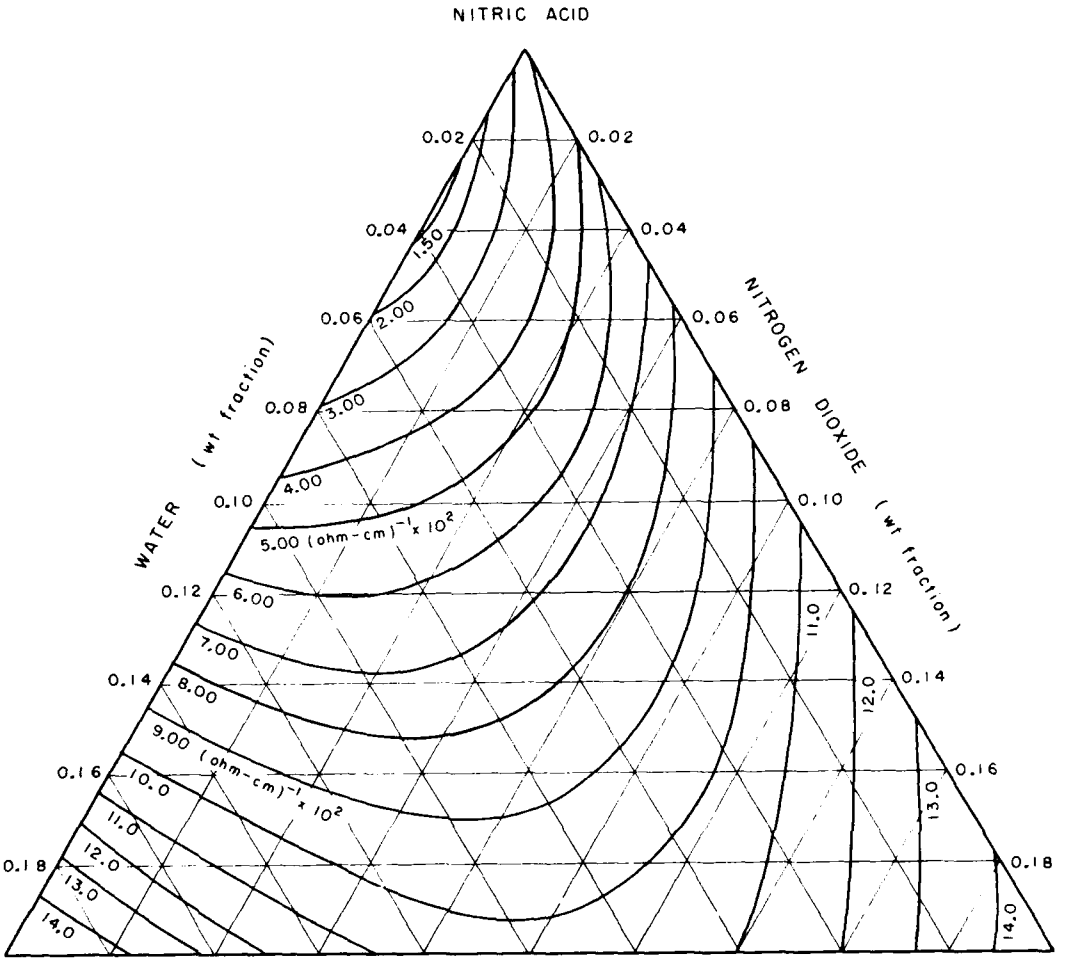

Figure 5. Curves of Constant Specific Conductance for Nitric Acid--Nitrogen Dioxide--Water at 32°F and Atmospheric Pressure

REFERENCES

1. Ostwald, W., "Über Apparate zur Bestimmung der elektrischen Leitfähigkeit von Elektrolyten," *Zeitschrift für physikalische Chemie*, 2:561-567, 1888.

2. Veley, V. H., and Manley, J. J., "Electric Conductivity of Nitric Acid," *Philosophical Transactions of the Royal Society of London*, A191:365-398, 1898.

3. Ingold, C. K., Hughes, E. D., and Reid, R. I., "Mechanism of Aromatic Nitration," *Journal of the Chemical Society*, 1950(September):2400-2440.

4. Goulden, J. D. S., and Millen, D. J., "Vibrational Spectra of Ionic Forms of Oxides and Oxyacids of Nitrogen," *Journal of the Chemical Society*, 1950(October): 2620-2627.

THIS REPORT HAS BEEN DISTRIBUTED ACCORDING TO SECTIONS A, C, AND DP OF JOINT ARMY-NAVY-AIR FORCE MAILING LIST NO. 16 DATED 15 JULY 1951